Indian J. Phys. **78B(2)**, 165–169 (2004)

AN INTERNATIONAL JOURNAL
IJP B

Microwave absorption and dielectric relaxation in 3-bromoaniline and its mixtures with 1-propanol in dilute solutions of benzene

V A Rana and A D Vyas[1]*

[1]Department of Physics, School of Sciences, Gujarat University, Ahmedabad-380 009, Gujarat, India

E-mail : ranava2001@yahoo.com

Received 14 November 2003, accepted 27 January 2004

Abstract : Complex permittivity (ϵ', ϵ'') at 9.1 GHz, static permittivity (ϵ_0) at 455 KHz and permittivity at optical frequency (ϵ_∞) of 3-bromoaniline, 1-propanol and their binary mixtures have been measured at different temperatures (20–47°C) in a non-polar solvent benzene. The measured values of permittivity and dielectric loss have been used to evaluate relaxation time and distribution parameter. The observed values of distribution parameter (α) for 3-bromoaniline and 1-propanol at different temperatures indicate more than one relaxation processes in these systems. The dielectric data for mixtures show interaction between the constituent molecules.

Keywords : Dielectric relaxation, relaxation time, distribution parameter, hydrogen bonding.

PACS No. : 77.22 Gm

1. Introduction

Dielectric relaxation in the mixtures of associative and non-associative molecules has evoked considerable interest, because in these systems, apart from self-association, there is a possibility of hetero association through hydrogen bonding. In this category of mixtures, the alcohol-amine systems have gained importance because both have proton donor and proton acceptor groups, further they are used in industries [1]. Garabadu and Swain [2] from the study of mutual correlation factor and excess parameters like molar polarization and excess free energy, observed dipolar interaction in mixtures of some long chain alcohols and aniline. From the viscosity and excess molar volumes for liquid mixtures of alcohol with amine, Oswal and Desai [3] suggested strong cross association due to hydrogen bonding between -OH and -NH_2 group. Similar results were obtained for the amine-alcohol mixtures by Tripathi *et al* [4] and Fattepur *et al* [5]. Recently, Abd-El-Nour and Abd-El-Messieh [6] studied dielectric relaxation mechanism of some aniline derivatives and the effect of such derivatives on self-association of some aliphatic alcohols (C_4–C_{10}). They found from dipole moment determination of these mixtures that in the case of N,N-diethyl aniline, the critical concentration at which hydrogen bond formation in the investigated alcohols is expected to be blocked, is inversely proportional to the number of carbon atoms. We studied [7,8] dielectric relaxation in mixtures of aniline, 2-chloroaniline, 3-chloroaniline, 4-fluoroaniline with 1-propanol using time domain spectroscopy in liquid state. These measurements show strong molecular association through hydrogen bonding between the constituent components of the mixtures. It was also observed that molecular association between aniline and alcohol mixture is affected by substitution of halogen group in aniline. In order to observe the effect of substitution of bromine in place of chlorine and flourine in aniline on dielectric properties of mixtures of 1-propanol with haloanilines, a systematic study of microwave absorption in aniline, 2-bromoaniline, 3-bromoaniline, 4-bromoaniline and their mixtures with 1-propanol in dilute solutions was conducted at different temperatures. 1-Propanol was taken as one of the constituent of the mixture because in our earlier studies, we found that self-association in 1-propanol takes place at higher concentration than in the case of methanol and ethanol in

*Corresponding Author

benzene solution. Therefore, the concentration range selected in present study is such that there is no self-association of 1-propanol. The results of study of 3-bromoaniline and its mixture with 1-propanol are presented in this paper. Our earlier reported results [9–11] on dielectric study of aniline, 2-bromoaniline, 4-bromoaniline and their mixtures with 1-propanol are also included here for comparison.

2. Experimental details

The samples of 3-bromoaniline (purum) supplied by Fluka A. G. (Switzerland) and 1-propanol (AR grade) supplied by Sd-Fine Chem Co. Ltd. (India) were used without further purification. Benzene (AR grade) supplied by Qualigens (India) was used after fractional distillation and drying over sodium. The mixtures of different compositions 3 : 1, 1 : 1 and 1 : 3 of 3-bromoaniline + 1-propanol were prepared by adding them by mole. These mixtures were taken as solute and added to non-polar solvent benzene. Five dilute solutions of each of these mixtures as well as individual molecules were prepared using benzene as non-polar solvent.

The dielectric permittivity (ϵ') and dielectric loss (ϵ'') for each polar molecules and their mixtures in benzene solutions at microwave frequency 9.1 GHz, were determined by the method suggested by Heston *et al* adopted for short circuited termination and described elsewhere [12]. The static permittivity (ϵ_0) at frequency 455 KHz was determined by resonance method, which uses a tuned oscillator circuit and a standard variable capacitor. ϵ_∞ was taken as square of refractive index, which was measured by Abbe refractometer. All the measurements were made at 20, 30, 40, and 47°C and the temperature was controlled within ±0.5°C by a thermostat. The most probable relaxation time (τ_0) and distribution parameter (α) of the polar molecules and their mixtures were determined using Higasi's single frequency method [13].

3. Results and discussion

Permittivity (ϵ') and dielectric loss (ϵ'') of solutions were plotted against concentration (weight fraction) of solute (3-bromoaniline and 1-propanol), the slope a_0, a', a'' and a_∞ of these plots for single component as well as for the mixtures at different temperatures are listed in Table 1. Values of relaxation time τ_0 and distribution parameter α for individual components (3-bromoaniline and 1-propanol) are presented in Table 2. In this table, earlier reported

Table 1. Values of a_0, a', a'' and a_∞ of 3-bromoaniline, 1-propanol a their mixtures in benzene solutions at different temperatures.

Temp.	a_0	a'	a''	a_∞
		3-Bromoaniline		
20	5.13	2.95	2.05	0.1
30	4.68	2.87	1.80	0.1
40	4.29	2.86	1.63	0.1
47	3.95	2.81	1.40	0.1
		1-Propanol		
20	5.64	4.78	1.26	-0.3
30	5.05	4.29	1.12	-0.4
40	4.60	4.05	0.98	-0.5
47	4.00	3.57	0.82	-0.5
		3 : 1 Mixture of 3-bromoaniline +1-propa		
20	6.20	3.30	1.94	0.2
30	5.60	3.10	1.84	0.2
40	5.10	2.88	1.74	0.1
47	4.70	2.70	1.57	0.0
		1 : 1 Mixture of 3-bromoaniline +1-propa		
20	5.86	3.41	1.78	0.1
30	5.33	3.24	1.65	0.1
40	4.93	3.10	1.43	0.1
47	4.46	2.83	1.24	0.0
		1 : 3 Mixture of 3-bromoaniline +1-propa		
20	6.20	3.60	1.60	-0.0
30	5.55	3.46	1.37	-0.1
40	4.80	3.20	1.17	-0.1
47	4.60	3.18	1.10	-0.1

Table 2. The relaxation time (τ_0) and distribution parameter (α) aniline, 2-bromoaniline, 3-bromoaniline, 4-bromoaniline, and propanol in benzene solutions at different temperatures.

Molecule	20°C		30°C		40°C		47°C	
	τ_0 in ps	α	τ_0 in ps	α	τ_0 in ps	α	τ_0 in ps	α
Aniline	4.4	0.11	4.2	0.11	4.1	0.11	4.0	0.0
2-Bromoaniline (2-BA)	8.5	0.09	6.9	0.09	5.8	0.11	5.2	0.0
3-Bromoaniline (3-BA)	14.9	0.11	13.1	0.13	11.4	0.12	9.7	0.1
4-Bromoaniline (4-BA)	14.6	0.24	13.0	0.21	12.5	0.22	11.1	0.2
1-Propanol	3.5	0.23	3.3	0.23	3.0	0.19	2.8	0.1

values of relaxation time (τ_0) and distribution parameter (α) for aniline, 2-bromoaniline and 4-bromoaniline [9–11] have also been included for comparison. Complex permittivity of aliphatic alcohols was measured by us [14] in dilute solutions of benzene and we observed deviation from linearity in the tanδ-concentration curve in concentration range 0.02 to 0.05 weight factor for alcohols investigated *i.e.* methyl alcohol, ethyl alcohol, 1-propanol and tertbutyl alcohol. For 1-propanol, it was about 0.04 weight factor. This indicates that at this concentration and above, the 1-propanol associate to form species other than monomers. In the present investigations, the concentration of 1-propanol in benzene was less than 0.04 weight factor and as shown in Figure 1, tanδ – concentration curve of 1-

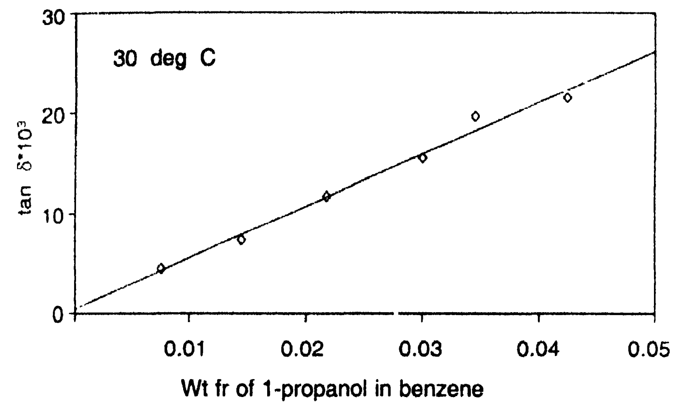

Figure 1. Plot of tan δ against concentration for solutions of 1-propanol in benzene at 30°C.

propanol in benzene solution at 30°C is linear. This indicates that below this concentration, there is no self-association of alcohols. The observed relaxation time of 1-propanol at 30°C is 3.3 ps, which is in agreement with our earlier studies [14]. The finite value of distribution parameter (α) for 1-propanol at all temperatures, suggests that at this frequency and dilution, predominant mode of relaxation in this system is due to rotation of -OH group around -C-O bond.

At 40°C, the relaxation time of 3-bromoaniline (11.4 ps) is higher than 2-bromoaniline (5.8 ps) and less than 4-bromoaniline (12.5 ps). This indicates that substitution of bromo group in orhto-, meta- and para-position with respect to amino group in aniline, increases relaxation time of these molecules. Nour and Messieh [6] from the dielectric loss measurement at the frequency range from 200 MHz up to 18 GHz, determined relaxation time for the overall molecular orientation for 2-, 3- and 4-bromoanilines and observed the similar results. Srivastava and Vij [15] studied dielectric relaxation in 2-, 3- and 4-chloroanilines at 25°C and observed a systematic increase in relaxation time with the shift of chlorine group from 2- to 3- and finally to 4-position with respect to amino group. They attributed this rise in relaxation time to effective change in length of dipoles. From Table 2, it can be seen that the relaxation time (τ_0) of 3-bromoaniline decreases with increase in temperature. This is usual behaviour of polar molecules in non-polar solvent. The value of distribution parameter (α) for 3-bromoaniline at 30°C is 0.13. This indicates that similar to aniline, there are more than one relaxation processes in 3-bromoaniline also *i.e.*, due to overall rotation and group rotation of $-NH_2$. The value of distribution parameter for 3-bromoaniline lies between the values of distribution parameter of 2-bromoaniline (0.09) and 4-bromoaniline (0.21), at the same temperature. This indicates that hindrance for intramolecular rotation of $-NH_2$ is greater in 2-bromoaniline and less in 3-bromoaniline and still less in 4-bromoaniline.

Dielectric data for mixtures of 3-bromoaniline + 1-propanol in dilute solutions of benzene was analyzed as single component system. The evaluated values of relaxation time (τ_0) and distribution parameter (α) for these mixtures at different temperatures are given in Table 3. It is evident from Table 3 that the relaxation time of the mixtures of 3-bromoaniline with 1-propanol, increases with an increase in concentration of 3-bromoaniline in the mixture at all temperatures. The plot of the relaxation time of the

Table 3. The relaxation time (τ_0) and distribution parameter (α) of the mixtures of 3-bromoaniline + 1-propanol in benzene solutions at different temperatures.

Molecule	20°C		30°C		40°C		47°C	
	τ_0 in ps	α	τ_0 in ps	α	τ_0 in ps	α	τ_0 in ps	α
1-Propanol	3.5	0.23	3.3	0.23	3.0	0.19	2.8	0.18
3-BA + 1-propanol (25–75%)	11.2	0.39	8.3	0.39	6.7	0.38	5.8	0.38
3-BA + 1-propanol (50–50%)	13.0	0.28	11.8	0.26	10.5	0.29	9.9	0.31
3-BA + 1-propanol (75–25%)	16.6	0.27	15.3	0.23	14.9	0.21	13.8	0.23
3-Bromoaniline	14.9	0.11	13.1	0.13	11.4	0.12	9.7	0.13

mixtures against the concentration of 3-bromoaniline at different temperatures is shown in Figure 2. This figure

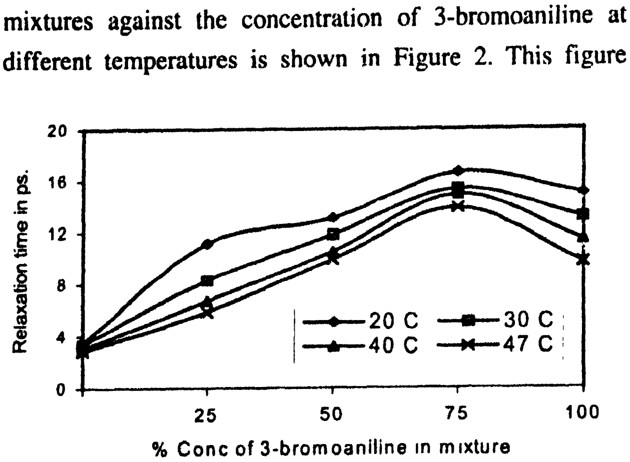

Figure 2. Variation of relaxation time of mixtures as a function of concentration of 3-bromoaniline in 1-propanol at different temperatures.

shows that the increase in relaxation time of the mixture with concentration of 3-bromoaniline is non-linear. In order to compare the present results and results of our previous studies on mixtures of aniline + 1-propanol [9], 2-bromoaniline + 1-propanol [10], 4-bromoaniline + 1-propanol [11], we plotted relaxation times of mixtures of anilines with 1-propanol against concentration of anilines. A typical plot of relaxation times of mixtures against concentration of anilines at 30°C is shown in Figure 3. It shows that

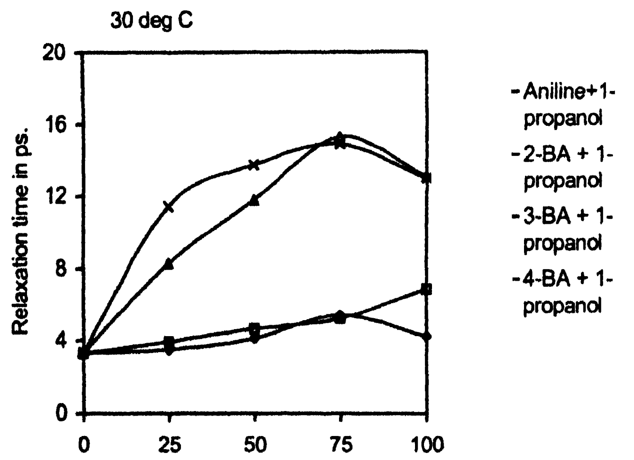

Figure 3. Variation of relaxation time of mixtures as a function of concentration of different anilines in 1-propanol at 30°C.

increase in relaxation time of the mixtures with concentration of anilines is non-linear. This indicates a solute-solute type of interaction between anilines and 1-propanol. Further, the maximum deviation in relaxation time occurs at 75% concentration of anilines in the mixture. This suggests that a strong molecular interaction between aniline and alcohol molecules is taking place in aniline rich region. The time domain dielectric measurements for mixtures of 2-chloroaniline, 3-chloroaniline and 4-fluoroaniline with 1-propanol obtained by us [7,8] in liquid state have shown similar results.

The distribution parameter of the mixtures of 3-bromoaniline with 1-propanol at different temperature and for all concentrations is higher than the distribution parameter value of its components. Further, it increases with the concentration of alcohol in the mixture and reaches maximum when the alcohol concentration is highest *i.e.* at 75% alcohol and 25% of aniline. The temperature variation of distribution parameter (α) of mixture at any concentration shows a negligible variation of this parameter with temperature. It appears that in these mixtures, there are solute-solute and solute-solvent interactions, providing a variety of local environments resulting in the domination of internal group rotation, which is usually independent of temperature. Rajyam *et al* [16] studied mixtures of propyl acetate and propanol and found a large value of distribution parameter. They attributed this rise due to formation of complexes *via* hydrogen bonding. The large values of distribution parameter for the mixtures of 3-bromoaniline and 1-propanol in the present study at all temperatures, also indicate formation of the complexes *via* hydrogen bonding between the constituent molecules.

Acknowledgment

The authors are thankful to Prof. V B Gohel, Head, Department of Physics, Gujarat University, Ahmedabad, for providing laboratory facilities and constant encouragement.

References

[1] R Sanghi *Resonance* **8** 17 (2003)

[2] K Garabadu and B B Swain *Indian J. Phys.* **68B** 271 (1994)

[3] S L Oswal and H S Desai *Fluid Phase Equil.* **161** 191 (1999)

[4] S Tripathi, G S Roy and B B Swain *Indian J. Pure Appl. Phys.* **31** 828 (1993)

[5] R H Fattepur, M T Hosamani, D K Deshpande and S C Mehrotra *J. Chem. Phys.* **101** 9956 (1994)

[6] Abd-El-Nour and Abd-El-Messieh *J. Mol. Liqs.* **79** 235 (1999)

[7] V A Rana, A D Vyas and S C Mehrotra *J. Mol. Liqs.* **102/1-3** 379 (2002)

[8] V A Rana, A D Vyas and N M More *Indian J. Pure Appl. Phys.* **40** 350 (2002)

[9] A D Vyas and V A Rana *Proceedings of the National Conference on Emerging Trends and Advances in Microwave Measurements and Techniques (NCMMT-2001), Aurangabad, India)* p79 (2001)

[10] A D Vyas and V A Rana *Proceedings of National Conference on Recent Advances in Microwaves, Antennas and Propagation (Microwave-2001, Jaipur,India)* p344 (2001)

[11] A D Vyas and V A Rana *Microwave Measurement Techniques and Applications* (ed) J Behari (New Delhi, India : Anamaya Publishers) p36 (2003)

[12] V A Rana *PhD Thesis* (Gujarat University, Ahmedabad, India) (2001)

[13] K Higasi *Bull. Chem. Soc.*(Japan) **39** 2157 (1966)

[14] A D Vyas and V M Vashsith *J. Mol. Liqs.* **38** 11 (1988)

[15] K K Srivastava and J K Vij *Bull. Chem. Soc.* (Japan) **43** 2307 (1970)

[16] B S Rajyam, C V Ramasastry and C R K Murty *Indian J. Pure Appl. Phys.* **18** 374 (1980)